

High Pressure Phase Transition and Behavior of Proton in Brucite $\text{Mg}(\text{OH})_2$

Various kinds of OH-related chemical species are included even in nominally anhydrous minerals. Even if there is a small amount of hydrous component in minerals, OH affects the physicochemical properties of minerals during geological reactions. Investigation of OH in minerals is an important theme for earth science.

The major geological reactions occur under conditions of high temperature and high pressure deep under the surface of the Earth, such as at the lower crust and mantle. From the interests of the behavior of OH or protons in minerals under conditions of high temperature and high pressure, infrared (IR) microspectroscopy with a high temperature diamond anvil cell (HTDAC) is a useful method to investigate a small quantity of hydrous components and the behavior of protons in minerals.

The crust and mantle of the Earth consist of rocks of which the chemical components are chiefly Si, Mg and O. Magnesium hydroxide $\text{Mg}(\text{OH})_2$ (mineral name: brucite) is a prototype of hydrous magnesium silicates because of its simple chemical composition and crystal structure. The behavior of brucite under high temperature and high pressure has been widely studied by X-ray and neutron diffraction and Raman and IR spectroscopy. In this article, we report on the IR absorption spectra of brucite under conditions of high temperature and high pressure, measured with an HTDAC and an IR microscope at beamline BL43IR [1].

A lever-type and externally heating HTDAC was settled on a pulse stage of 1 μm steps under the IR microscope of BL43IR. The ruby fluorescence technique was used for measuring pressure at an elevated temperature. A thermo-couple located very closely to a diamond was used for measuring

temperature. Fluorocarbon fluid (Fluorinert) was used as a pressure transmitting medium. A rhenium gasket of 250 μm thickness was preindented and drilled with a YAG laser (1064 nm). The IR spectra were measured with an LN_2 cooled InSb detector and a Bruker FTIR IFS 120 HR under the conditions of 4 cm^{-1} resolution and 512 scans. A natural clear single crystal of brucite from Zimbabwe was prepared. Two series of experiments using (001) platelet sample were carried out. The sample was pressurized at 25 $^\circ\text{C}$, and no further pressure was applied during the heating of the sample. Because of thermal expansion of HTDAC including pressure transmitting medium, the internal pressure was increased by heating with a fixed load.

The crystal structure of brucite is a CdI_2 type structure with MgO_6 octahedral layers (brucite layer) stacked along the c-axis and the OH dipole oriented normal to the brucite layers (Fig.1).

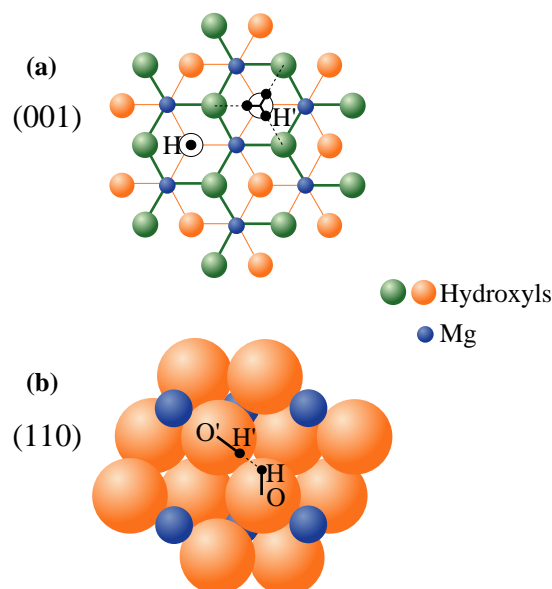


Fig. 1. Schematic crystal structure of brucite. (a) shows (001) view of brucite layer where an upper and lower hydroxyls are thick and thin lines. (b) shows a (110) horizontal view of layers. The original OH dipole is vertical to a brucite, and represented as an O-H dipole. The O'-H' dipole indicates a pressure induced OH dipole in brucite.

Although X-ray studies showed no phase transition involving Mg-O substructure under high pressure up to 30 GPa, a pressure induced IR absorption peak at 3650 cm^{-1} was observed at 10 GPa in a DAC study [2]. Shinoda & Aikawa [3] also observed the pressure induced absorption peak by DAC and polarized IR spectroscopy, and assigned it to a new OH dipole under pressure, suggesting that a phase transition of brucite involved only protons.

Figure 1 shows a schematic drawing of a new proton site of brucite under pressure. Figure 2(a) shows the IR absorption spectra of a (001) platelet single crystal of brucite from 0.1 MPa, 25°C to 8.2 GPa, 220°C . An absorption peak of the original OH dipole is observed at 3700 cm^{-1} under 0.1 MPa, 25°C . A pressure induced absorption peak appeared at 3650 cm^{-1} over 3 GPa at 25°C . The sample was pressurized up to 3.6 GPa and heated. Absorbance of the pressure induced peak increased on compression and decreased on heating. The position of the pressure induced peak shifted to a lower wavenumber on compression, suggesting enhanced hydrogen bonding between an OH dipole and the neighboring O. In heating, the pressure induced peak continued to be observed at 7.7 GPa, 160°C and disappeared at 8.2 GPa, 200°C . After cooling, the internal pressure remained at 7.9 GPa and the intense pressure induced peak appeared again.

Figure 2(b) shows IR absorption spectra up to 16.5 GPa, 360°C . In the higher pressure region, the pressure induced peak was observed at the higher temperature. The pressure induced peak can be observed under 320°C 16.3 GPa, it then disappeared at 340°C 16.0 GPa. The tiny peaks at 16.5 GPa 360°C are interference fringes between culet faces of diamonds. After cooling, pressure remained at 17.6 GPa and the intense pressure induced peak appeared again (17.6 GPa, 23°C). After depressing, the pressure induced peak disappeared and the original peak still remained.

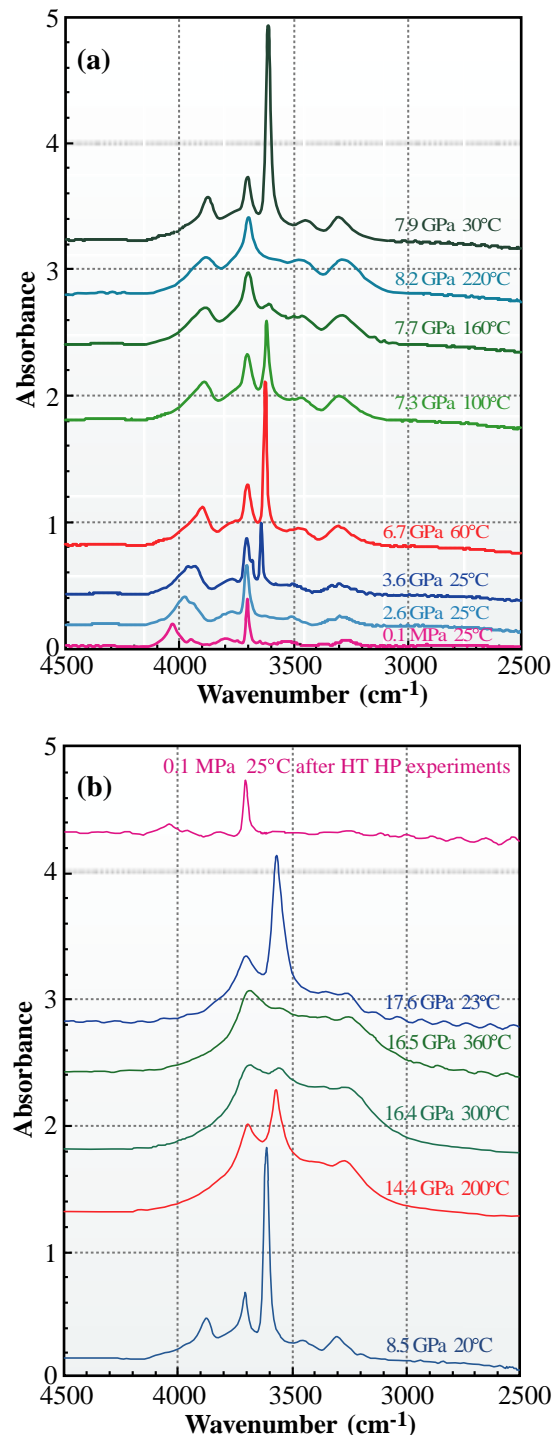


Fig. 2. IR absorption spectra of (001) platelet single crystal of natural brucite from Zimbabwe up to 8.2 GPa 220°C (a), and 16.5 GPa 360°C (b). An absorption peak at 3700 cm^{-1} is due to the original OH stretching motion and the pressure induced peak appears in the lower wavenumber side of the original.

As shown by the *in-situ* observations, the onset of the pressure induced peak is a reversible and unquenchable phenomenon and indicates a high pressure phase transition involving a new proton site. The formation process of the new OH dipole can be proton transfer between brucite layers. At ambient pressure, there is no interaction between the OH in a brucite layer and the O' of the next layer. By compression, the O...O' distance is shortened, and the energy levels of two neighboring OH groups overlap.

The activation energy of proton transfer to

adjacent oxygen is lowered by shortening the O...O' distance proton transfer is enhanced, and the resultant O'H' dipole is formed by proton transfer between donor OH and the nearest neighboring acceptors O' (Fig. 1).

In Fig. 3, solid circles and squares show the presence of the pressure induced peak, and the open ones do not show the presence of the pressure induced peak. Therefore, a boundary between the open and solid marks in Fig. 3 must be a phase boundary of brucite. The two proton state is stable in the high pressure region [4].

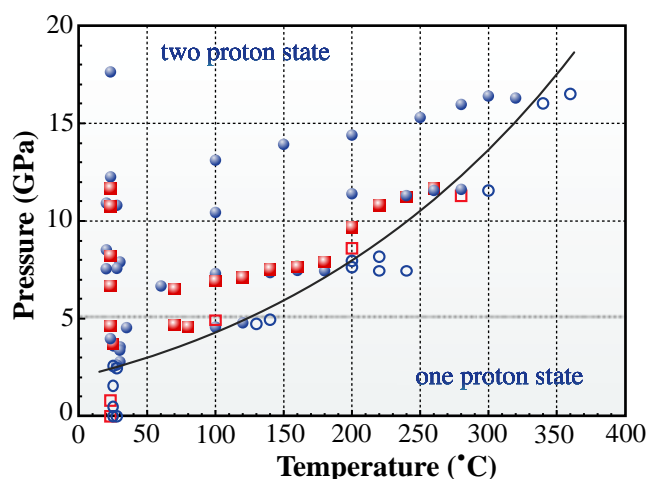


Fig. 3. The circles and squares represent two series of HT and HP experiments with (001) platelet single crystals of brucite. The points where the pressure induced peak was observed are represented by solid marks and the open ones show points where there was no pressure induced peak. A thick line indicates a phase boundary of brucite between the two proton and one proton states.

Keiji Shinoda

Osaka City University

E-mail: shinoda@sci.osaka-cu.ac.jp

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